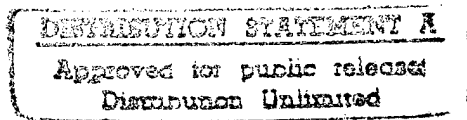


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1
2 **MAKING AGGREGATES AND ARTICLES MADE THEREFROM**
3

4 **Field of the Invention**

5 This invention pertains to the field of particulate materials
6 and articles made therefrom.
7

8 **Background of the Invention**

9 One prior art process of making an article from a
10 piezoelectric powder includes the steps of mixing the powder with
11 a few weight percent of a binder, often in a liquid solvent, to
12 form a slip; drying the slip to remove the solvent and to form
13 loose powder agglomerates containing dry binder; pressing the
14 agglomerates to form disks composed of powder particles held
15 together by the binder; and heat treating the disks to initially
16 burn out the binder at a lower temperature and then to grow
17 crystallites or crystals at a higher temperature. Porosity of
18 fully heat-treated or sintered disks is usually below 5%.

19 The disadvantage of this prior art process is that the disks
20 thus formed are difficult to make in large sizes.
21

22 **Summary of the Invention**

23 An object of this invention is a particulate raw material and
24 an inexpensive article made therefrom.

25 Another object of this invention is the use of a great deal
26 more of a binder than taught by the prior art.

1 Another object of this invention is a process and product,
2 which product has relatively large crystallites and high
3 piezoelectric properties.

4 Another object of this invention is an article made from
5 aggregates or granules which article has lower density and less
6 weight than a dense ceramic.

7 These and other objects of this invention are accomplished by
8 mixing powder composed of very small crystallites with in excess of
9 10% by weight of a binder to form a dried agglomerated powder; heat
10 treating the agglomerated powder to remove the binder and to grow
11 crystallites which are larger in size than the crystallites in the
12 starting powder to form a porous mass containing dense aggregates;
13 and cooling the porous mass. The porous mass is then broken up
14 into the aggregates to facilitate preparation of materials
15 therefrom which can be subsequently used to make an article.

16
17 Detailed Description of the Invention

18 The process described herein includes the steps of mixing a
19 powder with more than 10% by weight of a binder, based on the
20 weight of the powder and the binder, wherein the binder is
21 dissolved in a solvent to form a slip or the slip can be formed by
22 mixing a liquid binder and the powder; drying the slip to remove
23 the solvent to form dried, heavily agglomerated powder; heat-
24 treating the dried, agglomerated powder to drive-off the binder and
25 to grow crystallites to form a porous mass containing dense

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1 aggregates, which porous mass has a larger particle size and is
2 generally less dense than the initial powder. The slip can be
3 formed by mixing a liquid binder and the powder. Porosity of this
4 product is in excess of about 10% and the size of the crystallites
5 in the product is in excess of 1 micron.

6 The term "powder" is defined as a loose grouping or
7 aggregation of solid particles, usually smaller than 100 microns,
8 especially smaller than 10 microns. Many of such precursor powders
9 are commercially available and typically have an average particle
10 size of less than about 1 micron. Although any powder can be used
11 herein, preferred here are ceramic powders which, after compaction
12 and sintering, have piezoelectric properties with an average
13 crystallite size of up to about 100 microns.

14 Examples of the compositions of useful piezoelectric ceramic
15 powders include electrostrictive lead magnesium niobate titanate
16 (PMNT) and piezoelectric lead zirconate titanate (PZT) and barium
17 titanate (BaTiO_3). These are usually pre-reacted to form
18 homogeneous and stoichiometric compositions. If an electric field
19 causes a material to have a strain proportional to the square of
20 the field, then such a material is usually characterized as being
21 electrostrictive. If a material develops permanent polarization
22 and deforms more linearly with an applied field (at least with
23 lower applied voltages), the material is piezoelectric.
24 Electrostriction causes material deformation that is independent of
25 the polarity of the applied field. The electrostrictive material

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1 lead magnesium niobate titanate has the formula $0.9 \text{ Pb}(\text{Mg}_{1/3} \text{ Nb}_{2/3} \text{ O}_3)$
2 + 0.1 PbTiO_3 , whereas the piezoelectric material lead zirconate
3 titanate can have the formula $\text{Pb}(\text{Zr}_{0.52} \text{ Ti}_{0.48}) \text{ O}_3$.

4 In carrying out the process disclosed herein, a prereacted
5 powder is mixed with a binder to form a dispersion. The amount of
6 the binder on a weight basis is in excess of 10%, typically 20-80%,
7 and more typically 40-70%. Suitable binder is any material,
8 typically organic, that is essentially non-reactive with the
9 powder, which can bind the powder particles together and which can
10 be burned out or vaporized at a temperature below about 600°C ,
11 typically $100\text{--}500^\circ\text{C}$. A solid or a liquid binder is suitable which
12 can be dissolved or thinned in a suitable liquid solvent. Suitable
13 solvent is any liquid, typically organic or water, which can
14 dissolve or thin the binder and can be removed or be volatilized at
15 a temperature below about 150°C , typically near or below 100°C .
16 Specific examples of suitable binders are polymeric materials such
17 as polymethyl methacrylate resins, silicone rubbers, epoxy resins,
18 acrylic resins, polyvinyl alcohols and neoprene. Specific examples
19 of suitable solvents include hexane, toluene, ethane, acetone and
20 water.

21 The dispersion can be formed by mixing the powder with the
22 binder at room temperature or at an elevated temperature. The
23 binder is either dissolved or thinned by either dissolving or
24 mixing the binder beforehand with the solvent and then the
25 resulting binder solution is mixed with the powder. The dispersion

1 formed by mixing a powder with a binder solution is also referred
2 to herein as slip. The slip should have viscosity in the range of
3 10 to 1000 cps at room temperature in order to readily disperse
4 the powder in the binder. One percent or less, on weight basis, of
5 a dispersant can be added when preparing slip to reduce the
6 propensity for particle agglomeration.

7 In the preparation of the slip for manufacture of ceramic
8 articles such as transducers, the dispersion or mixing of the
9 binder solution and the powder is typically fully completed in
10 about one hour or less.

11 After the slip is prepared, it is subjected to a drying step
12 to remove the solvent. The drying step can be carried out by
13 heating the slip to a temperature below about 150°C, often below
14 100°C, for a period of time necessary to remove all or most of the
15 solvent. Duration of the drying step is dependent on the solvent
16 used and is typically from a fraction of one hour to a couple of
17 days, more typically from one-half hour to 24 hours. The drying
18 step can also be effected by other than conventional heating, such
19 as flash drying and freeze drying, in which case, drying duration
20 can be reduced substantially.

21 After drying the slip or removal of the solvent, the result is
22 a highly agglomerated dried powder wherein the powder particles in
23 the agglomerates are weakly held together by the binder. After
24 cooling, the agglomerated powder can be broken up into smaller
25 agglomerates, the size of which affects the size of the final

1 aggregates, and loaded into a suitable receptacle for heat
2 treatment. Since the agglomerated powder is weakly held together,
3 it can be broken up by manually crushing it into smaller
4 agglomerates. A suitable receptacle should be non-reactive with
5 the agglomerates that are loaded thereinto and made of a material
6 that can withstand the temperature of the heat treating step.
7 Suitable materials for the heat treating receptacle are alumina
8 (Al_2O_3) and zirconia (ZrO_2).

9 The heat treating step is conducted by heating from about room
10 temperature to a temperature range of up to about 1500°C, typically
11 about 300-1400°C. The heat treating step has two main objectives:
12 to remove or burn-out the binder and to grow and fuse the
13 crystallites. Although the heat treating step can be carried out
14 in two stages to separately accommodate binder removal and
15 crystallite growth, for practical reasons, it is often conducted in
16 one stage where the lower temperature heating is carried out at a
17 slower rate to remove the binder and the higher temperature heating
18 is carried out at a faster rate to minimize lead evaporation and to
19 provide for crystallite growth.

20 On the basis of the organic binders contemplated herein, the
21 binder will start to vaporize when the powder-binder mix is heated
22 to about 150°C and will be gone when the atmosphere is oxidizing
23 and a temperature of about 600°C is reached. Heating to remove the
24 binder should be done slowly at a rate of 5 to 50°C per hour,
25 typically 10-30°C per hour, to avoid cracking in the article made

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1 therefrom. In addition, a large volume of air should also be used
2 whereby partial pressure of oxygen in the air exceeds 1% by volume,
3 to prevent charring or deposition of carbon, preferably it should
4 not be in excess of about 10% by volume.

5 Once the binder is removed from the agglomerated powder, what
6 results are weakly bonded aggregates, composed of crystallites and
7 large pores or voids therebetween. Before sintering, the
8 crystallites in the aggregates are about the same size as in the
9 original powder, meaning that the crystallites have not yet grown.
10 Further heating after binder removal leads to growth of the
11 crystallites. This crystallite growth can be limited, where the
12 crystallites at least double in size, or can be on a larger scale
13 where the crystallites increase in size many times. With respect
14 to a piezoelectric powder, such as PZT powder having a sub-micron
15 initial average crystallite size, the final average crystallite
16 size can be in excess of 5 microns, particularly in the range of 8-
17 20 microns.

18 The crystallite growth takes place in the sintering
19 temperature range which depends on the initial powder employed. For
20 instance, the sintering temperature range for PZT powder is about
21 1180 to 1300°C and for barium titanate it is 1250 to 1380°C.
22 During the crystallite growth stage, the heat treating receptacle
23 should be sealed tightly to prevent loss of lead, if the original
24 powder contains lead as part of its composition.

25 On the basis of the powders contemplated herein, crystallite

1 growth can commence at about 400°C and can continue to about
2 1500°C. When pores between the crystallites are small, as when a
3 small amount of binder is used, diffusion can eliminate the pores,
4 however, when pores are large, as when a large amount of binder is
5 used, diffusion is insufficient to fill the large pores. Heating
6 in the crystallite growth region is typically conducted at a faster
7 rate than in the binder removal region. Heating to cause the
8 crystallites to grow can be conducted typically at a rate of 50-
9 500°C per hour, more typically 80-300°C per hour. What results
10 after the heat treating step is an easily broken up porous mass.

11 Such a porous mass is then cooled to nearly room temperature
12 at a rate typically corresponding to that of heating. The cooling
13 step is typically conducted at a rate of 50-500°C per hour, more
14 typically 80-300°C per hour. What results is a porous mass product
15 containing dense aggregates with the latter having a density of up
16 to about 8 g/cc, but more typically about 6-6.5 g/cc. The product
17 is often in a coherent mass which can be broken up by mild impact
18 to form the aggregates. These aggregates can be screened and used
19 to form an article.

20 The material prepared as described herein has larger
21 aggregates and as great a piezoelectric activity as the prior art
22 material. The last noted advantage applies to a material that has
23 a piezoelectric property.

24 Another advantage can be realized by the material prepared as
25 described herein if a very large amount of binder is used. If the

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1 amount of binder that is used to mix with the powder, especially
2 PZT powder, exceeds about 60% by weight, the product attains the
3 form of aggregates or granules, about 100-200 microns in size
4 individually, having porosity below 10%, typically 4-7%. This is
5 an important advantage since the impact and screening steps may be
6 dispensed with and the granules can be used to make an article,
7 such as a 0-3 composite transducer, where the larger size of the
8 granules compared to the powder particles in the disks or crushed
9 disks results in a 0-3 mode transducer that is less dense and has
10 a greater piezoelectric activity, assuming that a piezoelectric
11 powder was used initially.

12 Another advantage that can be realized by using the process
13 disclosed herein relates to relief of stress in crystallites.
14 Relief of stress in crystallites can lead to improved piezoelectric
15 performance in an article made from the granules. This embodiment
16 presupposes the use of a powder which has highly anisotropic
17 crystallites. This anisotropy arises during cooling. If such a
18 powder is sintered into a dense mass, the appearance of such an
19 anisotropy causes considerable stresses in such a mass, to the
20 point of it cracking and falling apart. Very few of such stresses
21 arise in a small granule, especially when it has low density. As a
22 result, 0-3 composite transducers made from such granules will have
23 improved piezoelectric performance over one made from stressed
24 material.

25 The granules prepared in accordance with the invention

1 disclosed herein, can be used to make an article, particularly an
2 electronic article, and more particularly a transducer. A 0-3
3 transducer can be made from a polymer matrix and from inclusions of
4 the ceramic granules distributed within the matrix. Based on the
5 combined weight of the polymer matrix and the ceramic granules,
6 amount of the ceramic granules in such transducers varies from 10%
7 to 50% by weight. This, of course, means that amount of the
8 polymer in such transducers is 90-50% by weight. In such 0-3
9 transducers, connectivity of the granules is zero and connectivity
10 of the polymer is three in the x, y and z planes. In 1-3
11 transducers, piezoelectric rods extend between electrodes with a
12 polymer resin disposed between the rods. In 1-3 mode, 0-3
13 transducers as discussed here, the ceramic granules are typically
14 greater than about 100 microns, more typically about 100-200
15 microns. The granules are simultaneously in contact with both top
16 and bottom electrodes and with the polymer surrounding the
17 granules. In 1-3 transducers, connectivity of the ceramic granules
18 is 1 and connectivity of the polymer is 3.

19 Transducers containing the ceramic granules disposed between
20 the electrodes and parallel to the poling direction, are generally
21 made by mixing a polymer with the ceramic granules and forming a
22 typically rectangular form with thickness typically of 50 to 500
23 microns, more typically 100 to 250 microns. Suitable polymers are
24 epoxy resins, polyurethane resins, acrylic resins, silicone
25 rubbers, and neoprene. Electrodes are provided on opposite

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1 surfaces of the form, as by painting a suitable metal paint, such
2 as a silver paint, or by sputtering thereon a metal, such as
3 silver. Electrodes can be 10-100 microns in thickness.

4 Prior art 0-3 transducers of this type made from lead titanate
5 obtained by breaking up sintered disks have a piezoelectric
6 activity or d_{33} of about 35-60 pC/N whereas 0-3 transducers made
7 with the ceramic granules and operating in the 1-3 mode are
8 expected to have d_{33} of about 65-100 pC/N, which is a significant
9 improvement. Furthermore, since the dielectric constant of a
10 material is affected by its density, reduced density of the
11 articles made with the new material will reduce its dielectric
12 constant. This is beneficial in the sensing mode.

13 The invention having been generally described, the following
14 examples are given as particular embodiments of the invention to
15 demonstrate the practice and advantages thereof. It is understood
16 that the examples are given by way of illustration and are not
17 intended to limit in any manner the specification or any claims
18 that follow.

19
20 Example 1

21 This example demonstrates preparation of granules about 100-
22 200 microns in size from a piezoelectric ceramic powder.

23 Pursuant to the disclosure herein, a binder solution was
24 prepared by dissolving 40 grams of solid polyvinyl alcohol binder
25 in 400 ml of water solvent at 75°C and 5 drops of Tamol®

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1 dispersant. The binder solution was prepared by stirring for 1
2 hour the ingredients on a hot plate. After the binder solution was
3 prepared, it was mixed with 20 grams of PZT-5H powder having
4 average particle diameter of 0.8 microns to form a slip which
5 contained 67% binder, on dry weight basis. The slip in a beaker
6 was dried by heating the beaker on a hot plate to about 100°C and
7 leaving overnight to drive-off water. After the slip was dried,
8 what resulted was a highly agglomerated dried powder wherein the
9 agglomerates were weakly held together, if at all.

10 The highly agglomerated dried powder was manually broken-up,
11 loaded into a zirconia (ZrO_2) boat receptacle and moved into a
12 burnout furnace. Removal or burn-out of the binder took place in
13 the furnace which was heated from room temperature to about 600°C
14 at a slow rate of slightly over 10°C per hour with air flowing
15 through the furnace at a rate sufficient to prevent charring.
16 Volatilization of the binder commenced at about 150°C and all of
17 the binder was gone when a temperature of about 500°C was reached.

18 The boat was then removed from the furnace and cooled to room
19 temperature. What was in the boat was a highly porous mass
20 containing crystals that were about the same size as the crystals
21 in the powder and large pores between the crystals. The matrix was
22 weak and could be easily crushed manually.

23 The boat was removed from the burnout furnace and cooled. It
24 was then sealed tightly with a zirconia plate to prevent loss of
25 lead and loaded into a sintering furnace where the boat and its

1 contents were heated from room temperature to 1280°C with a soak of
2 one hour at 1280°C. Since the binder was removed at a temperature
3 of below 600°C, the sintering furnace was quickly heated to about
4 500°C and then at a rate of 3°C per minute until 1280°C was
5 reached. During sintering, crystals grew in size and the product
6 became more dense. Following sintering, the boat was allowed to
7 cool at a rate of about 100°C per hour to room temperature.

8 The final product was a porous mass in the form of dense
9 aggregates or granules as large as 800 microns in size containing
10 crystals of about 10 microns in size. Its porosity was about 15%.

11
12 Example 2

13 This example demonstrates preparation of an article from the
14 granules similar to those of Ex. 1, above.

15 The granules used in this example have average diameter of 200
16 microns and their density is 6.3 g/cc.

17 A casting mold is used that consists of a wide groove, which
18 groove is rectangular in cross-section, 200 microns deep, 2
19 centimeters wide and 10 centimeters long. A dispersion is prepared
20 by mixing the granules with liquid methyl methacrylate binder. The
21 dispersion consists of, on weight basis, 25% granules and 75%
22 binder.

23 The groove in the casting mold is filled with the dispersion
24 and levelled. The methyl methacrylate binder in the groove is cured
25 by maintaining the casting mold at room temperature for about 24

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1 hours to solidify the composition in the groove. After the
2 solidified composition that takes the shape of the groove is
3 removed from the groove, its two major surfaces are painted with a
4 room temperature curing silver paint and the paint is allowed to
5 dry in 5-10 minutes in the room environment. The thickness of the
6 electrodes, i.e., the dried silver layer, is about 3 microns. The
7 result is a pressure sensitive film that can be used as a large
8 area pressure sensor with d_{33} of about 400 pC/N and d_h above 65
9 pC/N.

10 Many modifications and variations of the present invention are
11 possible in light of the above teachings. It is, therefore, to be
12 understood that the
13 invention may be practiced otherwise than as specifically
14 described.
15

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Abstract

The process for making a porous mass containing dense aggregates or granules includes the steps of mixing powder with more than 10% by weight of a binder to form agglomerated powder, heating the agglomerated powder to remove the binder and to grow crystallites in the powder to an average diameter exceeding 5 microns to form a porous mass containing the dense aggregates, and cooling the porous mass. The porous mass is broken up, if it is cohesive, into the aggregates containing the crystallites and the aggregates can be used to make an article, such as a transducer. The transducer is essentially a thick film and its thickness is that of the ceramic aggregates of granules. The electrodes connect to the top and to the bottom of the aggregates. As a result, the transducer material operates in the 1-3 mode.